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A Review on Luminescence properties in Eu Doped Phosphate Phosphors

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Abstract

In 1996, Matsuzawa *et al*. reported on the enormously long-lasting afterglow of $SrAl_2O_4$: Eu^{2+} co-doped with Dy^{3+} ions, which was more than 10-times brighter than the previously widely used ZnS: Cu. Since then, research for stable and efficient phosphors has constantly gained attractiveness. However, even today - almost 15 years after the invention of $SrAl_2O_4$: Eu^{2+} the number of luminescent materials is still comparatively low. Furthermore, the mechanism behind this phenomenon is still uncertain. Although most of the authors agree on the general features, such as the existence of long-lasting trap levels, many details are still shrouded in unknown. In this review, we present an outline of the important phosphate based phosphors of known luminescent materials based on Eu^{2+} doping and how they were prepared, and we take a closer look at the mechanisms and applications that have been suggested to explain bright afterglow in various compounds.

Keywords: Luminescence; europium; phosphorescent; rare -earths

1. INTRODUCTION

Luminescence is "cold light", light from other sources of energy, which can take place at normal and lower temperatures. In luminescence, some energy source kicks an electron of an atom out of its ground state into an excited state, then the electron gives back the energy in the form of light so it can fall back to its ground state [1-2]. Luminescent material is also called ‘phosphors’. The word ‘phosphor’ comes from the Greek language and means ‘light bearer’, to describe light-emitting or luminescent materials; barium sulfide is one of the earlier known naturally occurring phosphors. A phosphor is luminescent, that is, it emits energy from an excited electron as light. The excitation of the electron is caused by absorption of energy from an external source such as another electron, a photon or an electric field. An excited electron occupies a quantum state whose energy is above the minimum energy ground state. In semiconductors and insulators, the electronic ground state is commonly referred to electrons in the valence band, which is completely filled with these electrons. The excited quantum state often lies in the conduction band, which is empty and is separated from the valence band by an energy gap called the band gap, ΔE_g. Phosphors are solid luminescent material which emits photons when excited by an external energy source, such as electron beam or ultraviolet light. Phosphors are consists of a host lattice and a luminescent center often called as an “Activator”. The activator absorbs the exciting radiations and is raised to an excited state. The excited state returns to the ground state by emission of radiation. In some material the activator does not absorbs the excitation radiation but the other ion may absorb the exciting radiation and subsequently transfer it to the activator. In this case the absorbing ion is called as a sensitizer. In many cases the host lattice transfers the excitation energy to the activator, so the host lattice act as a “Sensitizer” [3]. The host lattice is constituted of at least one kind of oxide selected from the sulphide, aluminate, alumino silicate, silicate, tantalite, niobate, phosphate, halophosphate, Borate, tungstate etc.

In recent years, phosphate compounds have fascinated significant attention as plasma display panels (PDPs) materials due to the fact that phosphate-based phosphors are important luminescence host and have their strong absorption in VUV region (100–200 nm), and also have a high chemical stability and inexpensive cost. Phosphate phosphors are one of the most important luminescence materials because of their excellent high physical and thermal stability and long afterglow and high brightness as well as lower temperature synthesis. Among them, Eu^{2+}-activated $ABPO_4$ phosphors (A and B are mono- and divalent cations, respectively) have been reported as blue-emitting phosphors excited by near UV- LEDs. For instance, $KSrPO_4:Eu^{2+}$, $KBaPO_4:Eu^{2+}$, and $LiCaPO_4:Eu^{2+}$ have excellent luminescence properties including quantum efficiency and thermal quenching behavior. Therefore, they are considered to be potential application as phosphors for the white light emitting diodes [4]. In this article we presented a review on Eu^{2+} doped different phosphate compounds.

2. MATERIALS AND SYNTHESIS TECHNIQUES

In this paper we have discussed several kinds of methods and materials which have been synthesized already. Some of them are listed in Table 1.

Table 1. Eu^{2+} based phosphate luminescent materials

Synthesized Phosphors	Starting Precursors	Synthesis Method	References
$LiCaPO_4$: Eu^{2+}	$LiNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$ $Eu(NO_3)_3$,	Polymerizable complex (PC) method	4
$KLa_{1-x}Eu_xP_4O_{12}$	K_2CO_3, La_2O_3 , $NH_4H_2PO_4$, Eu_2O_3	Co-precipitation method	5
$Mg_{21}Ca4Na4(PO4)_{18}$	$Mg(NO_3)$, $Ca(NO_3)_2$ $NaNO_3$, $NH_4H_2PO_4$	Combustion-assisted synthesis technique	6
$Ca_4(PO_4)_2O$	$CaCO_3$, $NH_4H_2PO_4$, Eu_2O_3 and CeO_2	solid-state method	7
$Na_2CaP_2O_7$: RE^{3+}	Na_2CO_3, $CaCO_3$, NH_4 H_2PO_4, $(NH_4)_2Ce(NO_3)_6$, Tb_4O_7, Sm_2O_3 and Eu_2O_3	Solid state reaction method	8
$Sr_5(PO_4)_3F$: Eu^{3+}	$Sr(NO_3)_2$, $NH_4H_2PO_4$, NH_4F, Eu_2O_3	Combustion synthesis	9
$KSrY(PO_4)_2$: Eu^{2+}	K_2CO_3, $SrCO_3$, $Y2O_3$, $NH_4H_2PO_4$, and Eu_2O_3	Amorphous metal complex method and solid state reaction method	10
$LaPO_4$	La_2O_3, $[(NH_4)_2H\ PO_4)]$, Ce_2O_3 and Tb_4O_7	Solid state synthesis method.	11
$Li_2Zr(PO_4)_2$	Li_2CO_3, ZrO_2, $NH_4H_2PO_4$ and Eu_2O_3	Solid-state reactions	12

3. KNOWN AND INVESTIGATED COMPOUNDS

A wide variety of host materials are used as luminescent compounds, but when it comes to persistent luminescence, the number of known hosts is relatively low. The majority of research on this phenomenon is concentrated around the phosphate, with

$Na_2CaP_2O_7$: $RE^{3+}$and $Mg_{21}Ca_4Na_4(PO4)_{18}$ as most famous representative. Besides these two main classes of materials, only few host crystals have been found to exhibit luminescence behavior with Eu^{2+} activators.

In this paragraph, we will present an overview of the compounds where Eu^{2+}-based luminescence has been reported. These materials are often labeled as "phosphorescent", but the definition of phosphorescence is rather uncertain, since the term is also used for luminescence where a quasi-stable state is complex, causing an increased lifetime of the fluorescence decay. However, even the decay from such a quasi-stable state generally does not last longer than a second [13].

The spectroscopic properties $KLa_{1-x}Eu_xP_4O_{12}$ nano-crystals were investigated by Marciniak et al. [5]. It was found that the intensity of the ligand-to-metal CT band in the excitation spectra decreases with increasing Eu^{3+} concentration in contrast to the CT emission intensity demonstrating strong concentration quenching. The CT emission decay times undergo a significant shortening with increasing dopant concentration. These phe- nomena were discussed in terms of the energy transfer from CT state to $4f^n$ states with increasing Eu^{3+} concentration due to the overlap between CT emission and $4f^n$ absorption bands of Eu^{3+}. It was found that CT band intensity decreases proportional to $1/N^2$, where N is the concentration. The strong dependence of CT intensity on Eu^{3+} concentration is significantly important for design of new light sources based on Eu^{3+} doped systems.

Eu^{2+}, Tb^{3+}, Mn^{2+} ions tri activated $Mg_{21}Ca_4Na_4(PO_4)_{18}$ (MCNP) phosphors have been synthesized by Zhang et al. [6]. The structure of MCNP in the trigonal space group R-3 contains three crystallographic sites of Ca^{2+} ions which could be replaced by Eu^{2+} ions. Under UV excitation, MCNP: Eu^{2+} shows a blue emission with a broad asymmetric band which can be well- decomposed into three Gaussian profiles which correspond to these three kinds of Ca^{2+} ions. The ET mechanisms from Eu^{2+} to Tb^{3+} ions and from $Eu^{2+}$to Mn^{2+} ions in the MCNP host have been certified to be dipole–dipole interaction and quadrupole–quadrupole interaction, respectively. Also, their critical distances were calculated by using the concentration quenching method. Sensitized by Eu^{2+} ions, theTb^{3+} and Mn^{2+} can emit intense green and red light at 550 and 645 nm, respectively. The color tunable emission can be realized by coupling the emissions bands centered at 425, 550, and 645 nm due to the contribution from Eu^{2+} and Tb^{3+} and Mn^{2+}, respectively. These results show that the as-prepared MCNP: Eu^{2+}, Tb^{3+}, Mn^{2+}phosphors with tunable white emission could find applications in the area of UV-converted white LEDs.

Yinqun et al. [7] have reported the experimental results described that the $Ca_4(PO_4)_2O$:0.1Ce^{3+}/Li^+, 0.06 Eu^{2+} phosphor had two emission bands located at blue region and yellow region under the excitation of UV light. $Ca_4(PO_4)_2O$: 0.1 Ce^{3+}/Li^+, 0.06 Eu^{2+}could be systematically tuned to generate white light under different excitation wavelengths. This study revealed that $Ca_4(PO_4)_2O$:0.1Ce^{3+}/Li^+,0.06Eu^{2+} phosphor might have potential applications as a single-phase white-emitting phosphor for UV white LEDs.

The luminescent properties of Eu^{3+} doped and Li^+ co-doped $Sr_5(PO_4)_3F$ phosphate based phosphor phosphors were investigated. by Shinde et al. [9]. The formation of homogeneous single phase lamp phosphors not only demonstrates the capability of the combustion process in the atomic level doping of impurity ions in the host lattices but also confirms the highly exothermic nature of combustion. The major advantages of the combustion process are improvement in processing time, energy saving and the fine particle nature of the combustion products. Under the excitation around 395 nm, the $Sr_5(PO_4)_3F$: Eu^{3+} phosphors show the red/orange emission from Eu^{3+}. The luminescence intensity of $Sr_5(PO_4)_3F$: Eu^{3+} was significantly enhanced by co-doped with Li+, probably due to the charge compensation. This elementary work can be important in developing new luminescent devices applicable for tricolor lamps, light emitting diodes and other fields.

$LiCaPO_4$: Eu^{2+} phosphor with high photoluminescence was synthesized by Kim et al. [4] using a polymerizable complex (PC) method employing a water-soluble polyethylene glycol-conjugated phosphate ester (PEG-P). PEG-P could be obtained from a reaction among polyethylene glycol 300, phosphorus pentoxide, and pyrophosphoric acid. The PEG-P prepared was stable in an aqueous condition. A transparent solution and gel were obtained when the PEG-P was used as a source of P during the PC method, whereas the use of H_3PO_4 caused an undesirable precipitate. The $LiCaPO_4$: Eu^{2+} obtained via the PC method employing the PEG-P showed higher emission intensity than those synthesized by a solid state reaction method and the PC method employing H_3PO_4. The high luminescence properties of the sample synthesized using the PEG-P may be attributed to high homogeneity of constituents in the sample.

The luminescence characteristics were evaluated by synthesizing Eu^{2+} doped samples for phosphates of various compositions by Saito et al. [10]. The study led to a green light emitting $KSrY(PO_4)_2$:Eu^{2+}, which is rare for a phosphate phosphor. $KSrY(PO_4)_2$:Eu^{2+} had an excitation band between 250 and 450 nm and emitted green light, reaching an emission maximum at 520 nm. This suggests that excitation by a near-ultraviolet LED is possible, $KSrY(PO_4)_2$:Eu^{2+} could be useful as a phosphor for white LEDs.

$LaPO_4$ phosphor doped with Eu and Tb rare-earth ions, keeping Eu concentration constant and varying Tb concentration as 0.1, 0.5 and 1.5% were prepared using solid state synthesis method are successfully synthesized by Patil et al [11]. The main peak in XRD pattern was found around 28.5^0 corresponding to a d-value of about $3.11A^0$, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate. As the Tb concentration increases the PL intensity also increases. The PL intensity is very high therefore; the LaPO4: Eu,Tb phosphors can be easily applied in various types of lamp and display.

4. CONCLUSION

In this review article we have discussed Eu activated different phosphate phosphors. The search for new and enhanced materials with Eu^{2+} ions as activators continues and has recently turned to other host materials, based on the developments in LED conversion phosphors. Additionally, the quest to unpick the mechanism behind the luminescence has entered a new path. Various models have been proposed in the past few decades with only a small amount of experimental backup, but only recently researchers have started applying new and promising techniques that could confirm or contradict these theories. A better understanding of the exact mechanism is crucial for the development of practical applications such as emergency lights, traffic signals, dials and displays, textile printing, medical diagnostics etc. Eu^{2+} activated long-lasting phosphors will play a very important role in the bright future of luminescence technology.

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